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BIS(η-ISOPROPYLCYCLOPENTADIENYL)TANTALUM CHEMISTRY: SOME HYDRIDE, CARBONYL, ALKYL, ALKYNE AND TERTIARYPHOSPHINE DERIVATIVES, AND AN IMPROVED SYNTHESIS OF DICHLOROBISCYCLOPENTADIENYLNIOBIUM

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Summary

The new compounds [Ta]Cl_2, [Ta]H_3, [Ta]H(CO), [Ta]Cl(CO), [Ta]Cl(PMe_3); [Ta]Me(PMe_3) and [Ta]Cl(Me_2C_2), where [Ta] = Ta(η-i-PrC_5H_4)$_2$, are described. Nb(η-C_5H_5)Cl_2 is synthesised in high yield from Nb(η-C_5H_5)Cl_4 and $C_5H_5Sn(n\text{-}Bu)_3$.

We have long been interested in the chemistry of the η-cyclopentadienyl derivatives of the metals Nb, Ta, Mo and W and the study of compounds in this class has led to increased understanding of fundamental aspects of organotransition metal reactions, see for examples references 1—4.

Although the bis-η-cyclopentadienyltantalum system has been known since 1961 [5] it is only recently that convenient starting compounds have become available [6,7]. As a result the bis-η-cyclopentadienyltantalum system is comparatively little explored compared, for example, with the analogous tungsten system. Here we describe new chemistry of bis-σ-isopropylcyclopentadienyltantalum. The bulky alkyl ring substituent was chosen since there was previous evidence that this would result in enhanced thermal stability of compounds and, also in increased solubility.

Chemical studies

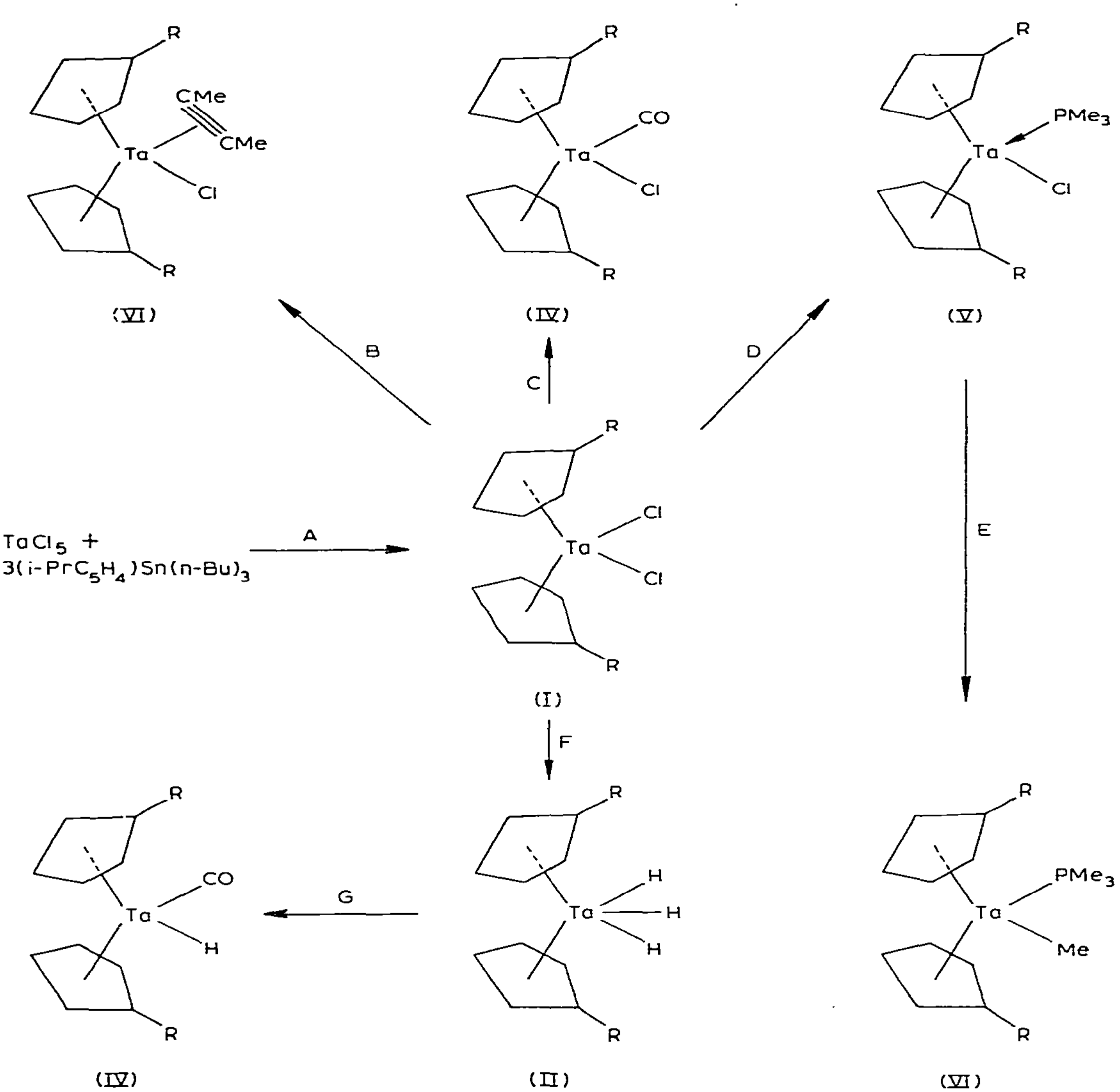
Treatment of tantalum pentachloride in dichloromethane with isopropyltri-n-butyltin in molar ratio 1 : 3 gives a smooth reaction and the dichloride Ta(i-PrC_5H_4)$_2Cl_2$ (I) may be isolated to over 70% yield. The compound I is soluble in toluene and dichloromethane. Both the pure compound and solutions are stable in air for periods of hours. Treatment of I in toluene with Na[AlH_2(OCH_2CH_2OMe)$_2$] causes formation of the trihydride [Ta(i-PrC_5H_4)$_2H_3$] (II) in up to 76% yield. The compound II readily recrystallised from toluene: petro-

TABLE 1

ANALYTICAL AND SPECTROSCOPIC DATA

Compound	Colour	Analytical data (%) [a]			Selected Mass [b] Spectral Data	^{1}H NMR data [c]
		C	H	Cl		
Ta(η-i-PrC$_5$H$_4$)$_2$Cl$_2$ (I)	deep green	40.5 (40.5)	4.6 (4.7)	16.0 (15.8)	465 (42, *P*) 430 (4, *P*—Cl) 358 (4, *P*-i-PrC$_5$H$_4$)	
Ta(η-i-PrC$_5$H$_4$)$_2$H$_3$ (II)	white	46.2	5.9 [d]			5.15 ($\underline{8}$, $\underset{\sim}{c}$, 2 C$_5$H$_4$); 7.23 ($\underline{2}$, $\underset{\sim}{c}$, 2 CH); 8.78 ($\underline{12}$, $\underset{\sim}{d}$, 4 Me); 10.47 ($\underline{1}$, $\underset{\sim}{t}$, Ta—H central); 12.45 ($\underline{2}$, $\underset{\sim}{d}$, 2 Ta—H) not central).
Ta(η-i-PrC$_5$H$_4$)$_2$H(CO) (III)	red	47.6 (48.2)	5.6 [e] (5.5)		424 (29, *P*) 492 (100, *P*—CO)	5.50 ($\underline{8}$, $\underset{\sim}{c}$, 2 C$_5$H$_4$); 7.42 ($\underline{2}$, $\underset{\sim}{c}$, 2 CH); 8.83 ($\underline{12}$, $\underset{\sim}{c}$, 4 Me); 16.20 ($\underline{1}$, $\underset{\sim}{s}$, Ta—H).
Ta(η-i-PrC$_5$H$_4$)$_2$Cl(CO) (IV)	yellow-green	44.4 (44.5)	5.0 (4.8)	7.5 [f] (7.7)	458 (11, *P*) 430 (100, *P*—CO)	5.20—5.80 ($\underline{8}$, $\underset{\sim}{c}$, 2 C$_5$H$_4$); 7.33 ($\underline{2}$, $\underset{\sim}{c}$, 2 CH); 8.8 ($\underline{12}$, $\underset{\sim}{c}$, 4 Me).
Ta(η-i-PrC$_5$H$_4$)$_2$Cl(PMe$_3$) (V)	red	44.2 (45.0)	5.8 (6.2)	6.7 (7.0)	506 (0, 1, *P*) 430 (4, *P*—PMe$_3$)	4.95, 5.30, 6.25 ($\underline{8}$, $\underset{\sim}{c}$, 2 C$_5$H$_4$); 7.50 ($\underline{2}$, $\underset{\sim}{c}$, 2 CH); 8.65 ($\underline{12}$, $\underset{\sim}{m}$, 4 Me); 8.90 ($\underline{9}$, $\underset{\sim}{s}$, PMe$_3$).
Ta(η-i-PrC$_5$H$_4$)$_2$Cl(C$_2$Me$_2$) (VI)	white	48.5 (48.5)	5.7 (5.8)	7.3 (7.3)	484 (0, 1, *P*) 430 (100, *P*—Me$_2$C$_2$)	4.40, 4.95 ($\underline{8}$, $\underset{\sim}{c}$, 2 C$_5$H$_4$); 7.45 ($\underline{8}$, $\underset{\sim}{c}$, 2 CH + 2 Me); 8.9 ($\underline{12}$, $\underset{\sim}{c}$, 4 Me).
Ta(η-i-PrC$_5$H$_4$)$_2$Me(PMe$_3$) (VII)	red	[g]			486 (16, *P*) 471 (11, *P*—Me) 410 (30, *P*—PMe$_3$)	5.55, 5.83, 6.0 ($\underline{8}$, $\underset{\sim}{c}$, 2 C$_5$H$_4$); 7.70 ($\underline{2}$, $\underset{\sim}{c}$, 2 CH); 8.75 ($\underline{12}$, $\underset{\sim}{c}$, 4 Me); 8.95 ($\underline{9}$, $\underset{\sim}{d}$(J(P—H)7) PMe$_3$); 10.45 ($\underline{3}$, $\underset{\sim}{d}$, (J(P—H)8) TaMe).

[a] Calculated values given in parenthesis. [b] Given as: *m/e* of peak for principal isotope (relative intensity (%), assignment) *P* indicates parent ion. [c] Given as: chemical shift (τ) (relative intensity, multiplicity (J in Hz), assignment). In C$_6$D$_6$. [d] ν(Ta—H) 1740s cm^{-1}. [e] ν(CO) and ν(Ta—H) 1865s, 1780m cm^{-1}. [f] ν(CO) 1885 cm^{-1}. [g] very sensitive to oxidation.



SCHEME 1

R = i-Pr. A) Room temperature in CH_2Cl_2 for 4 d, 72%. B) Na/Hg and Me_2C_2 in toluene, 58%. C) Na/Hg and 1 atm CO in toluene, 91%. D) Na/Hg and PMe_3 in toluene, 52%. E) MeLi in Et_2O at room temperature 55%. F) $NaAlH_2(OCH_2CH_2OMe)_2$ in toluene at room temperature 76%. G) CO (1 atm) at 150°C in nonane, 91%.

leum ether mixtures. Solutions of II in nonane are stable up to 150°C. Photolysis of II in toluene or ethylacetate using a medium-pressure mercury lamp cause no decomposition and the starting compound is recovered. Treatment of II with a carbon tetrachloride: chloroform mixture cause reduction to the dichloro derivative I. When a refluxing solution of nonane is treated with one atmosphere of carbon monoxide slow formation of the monocarbonyl $[Ta(\eta\text{-}i\text{-}PrC_5H_4)_2(CO)H]$ (III) occurs, eventually giving a 91% yield. Treatment of II with n-butyllithium in hexane gives no evidence for reaction and treatment of the reaction mixture with deuterium oxide recovers undeuteriated II. This observation contrasts with the formation of a lithio-tantalum compound on treatment of the compounds $Ta(\eta\text{-}RC_5H_4)_2H_3$ (R = H, Me) with n-butyllithium [7]. The compound II does not react with i-PrMgBr in diethylether: contrast the formation of tungsten-magnesio derivatives from $[W(\eta\text{-}C_5H_5)_2H_2]$ and i-PrMgBr [8].

Reduction of the compound I with magnesium amalgam in the presence of carbon monoxide, trimethylphosphine or 2-butyne affords the trivalent compounds $Ta(\eta\text{-i-}PrC_5H_4)_2LCl$, where L = CO (IV) Me_3P (V) or MeCCMe (VI) respectively. The compounds IV and V are highly sensitive to oxidation. Treatment of V with methyllithium gives the methyl derivative $[Ta(\eta\text{-i-}PrC_5H_4)_2Me(Me_3P)]$, VII. Treatment of the compounds IV, V, or VI with hydrogen chloride gives an oil which rapidly decompose at room temperature forming I. The nature of the oil is unknown, possibly it is $Ta(\eta\text{-i-}PrC_5H_4)_2HCl_2$. The data characterising the new compounds I—VII are given in Table 1, and do not require further discussion.

During the course of this work we reinvestigated the reaction between cyclopentadienyltri-n-butyltin and $[Nb(\eta\text{-}C_5H_5)Cl_4]$ [9] and found that when a suspension of this compound in dichloromethane is treated with $CpSn(n\text{-}Bu)_3$ the product in 79% yield is $Nb(\eta\text{-}C_5H_5)_2Cl_2$ (VIII). This reaction, therefore, represents much the simplest method of synthesis of the dichloro compound VIII.

The structure proposed for the new compounds I—VII are shown in Scheme 1. For the most part the bis(η-isopropylcyclopentadienyl)tantalum seems to resemble quite closely the unsubstituted analogue [10,11]. However, the two isopropyl groups appear to slow down reaction rates both towards formation and decomposition of compounds. It is interesting that the trihydride III is stable to photolysis and to substitution of a hydrogen by lithium.

Experimental

All reactions and manipulations were carried out under vacuum or in an inert atmosphere. Solvents were rigorously dried and distilled before use. ^1H NMR spectra were determined using a Perkin Elmer RB12. IR spectra were determined on mulls using a Perkin Elmer 457 spectrometer. (σ-Isopropylcyclopentadienyl)tri-n-butyltin was prepared by reaction between $i\text{-}PrC_5H_4Na$ and $Cl(n\text{-}Bu_3)Sn$ as described elsewhere [12]. Mass spectra were measured using an A.E.I. MS9 spectrometer.

Dichlorobis(η-isopropylcyclopentadienyl)tantalum, I

A suspension of tantalum pentachloride (30 g, 83.6 mmol) in dry dichloromethane (800 cm^3) was treated with pure $(i\text{-}PrC_5H_4)(n\text{-}Bu_3)Sn$ (115 g, 290 mmol). The mixture was stirred at room temperature for 4 days giving a deep green solution. This was concentrated under reduced pressure and petroleum ether (40—60°C) was added to the concentrate. Cooling (—20°C) gave deep green crystals which were collected, washed with petroleum ether (40—60°C) and dried in vacuo (yield, 28.1 g, 72%).

Trihydrobis(η-isopropylcyclopentadienyl)tantalum, II

The compound $[Ta(\eta\text{-i-}PrC_5H_4)_2Cl_2]$ (4.85 g, 10.3 mmol) in toluene (100 cm^3) was treated with $Na[AlH_2(OCH_2CH_2OMe)_2]$ (7 cm^3 of a 70% solution in benzene). The mixture was stirred at room temperature for 1 h, then hydrolysed at 0°C by addition of water (5 cm^3) in a dropwise manner. The mixture was filtered and the solvent was removed from the filtrate under reduced pressure. The residue was extracted with petroleum ether (40—60°C) (150 cm^3) and after filtration the filtrate was cooled (—70°C) giving white needle crystals. These were collected, washed with cold petroleum ether (30—40°C) and dried in vacuo (Yield, 3.1 g, 76%).

Carbonylhydridobis(η-isopropylcyclotadienyl)tantalum, III

A solution of Ta(η-i-PrC$_5$H$_4$)$_2$H$_3$ (1.71 g, 4.3 mmol) in nonane (30 cm^3) at 150°C was treated with carbon monoxide at atmospheric pressure for 4 h. The resulting red solution was cooled and the solvent was removed under reduced pressure. The residue was extracted with petroleum ether (40—60°C, 100 cm^3) and, after filtration the filtrate was cooled (—70°C) giving purple-red crystals. These were collected, washed with cold petroleum ether (30—40°C) and dried in vacuo (yield, 1.66 g, 91%).

Carbonylchlorobis(η-isopropylcyclopentadienyl)tantalum, IV

The compound [Ta(η-i-PrC$_5$H$_4$)$_2$Cl$_2$] (4.68 g, 10 mmol) in toluene (50 cm^3) was stirred with magnesium amalgam (92 g of 0.6% solution) under carbon monoxide at 25 psi. After 20 h the mixture was filtered and the solvent was removed from the filtrate under reduced pressure. The residue was extracted with warm petroleum ether (40—60°C, 180 cm^3) and the extract was filtered. The filtrate was concentrated under reduced pressure and cooled to —20°C. Yellow-green crystals separated which were collected, washed with cold petroleum ether (30—40°C) and dried in vacuo (yield, 2.98 g, 65%).

Chloro(trimethylphosphine)bis(η-isopropylcyclopentadienyl)tantalum, V

The compound Ta(η-i-PrC$_5$H$_4$)Cl$_2$ (3.78 g, 81 mmol) in toluene (70 cm^3) and trimethylphosphine (4.1 g, 5.4 mmol) was stirred with magnesium amalgam (11.0 g of a 0.6% solution) for 20 h. The pure products were isolated and crystallised from petroleum ether (30—40°C) at —20°C as described for the carbonyl analogue (yield, 2.1 g, 52%).

But-2-ynechlorobis(η-isopropylcyclopentadienyl)tantalum, VI

The compounds Ta(η-i-PrC$_5$H$_4$)$_2$Cl$_2$ (0.52 g, 1.1 mmol) and but-2-yne (0.5 cm^3, 7 mmol) in toluene (30 cm^3) were stirred with magnesium amalgam (65 g of a 0.6% solution) for 20 h. The pure compound was isolated as described for the carbonyl analogue as white crystals (yield, 0.31 g, 58%).

Methyl(trimethylphosphine)bis(η-isopropylcyclopentadienyl)tantalum, VII

The compound Ta(η-i-PrC$_5$H$_4$)$_2$(PMe$_3$)Cl (0.77 g, 1.5 mmol) in ether (50 cm^3) was treated with methyllithium (2 cm^3 of a 1.4 *M* solution in ether). The mixture was stirred for 4 h and then the solvent was removed under reduced pressure and the residue was taken up in petroleum ether (70 cm^3, 40—60°C). The extract was filtered, concentrated under reduced pressure and cooled to —78°C giving red crystals which were collected, washed with cold petroleum ether (30—40°) and dried in vacuo (yield, 0.4 g, 55%).

Dichlorobis(σ-cyclopentadienyl)niobium, VIII

The compound $[Nb(\eta\text{-}C_5H_5)Cl_4]_n$ (2.05 g, 6.8 mmol) prepared as described, [6], was suspended in dichloromethane (150 cm^3) and the mixture was treated with pure $(\sigma\text{-}C_5H_5)(n\text{-}Bu)_3Sn$ (6.35 g, 18 mmol). The mixture was stirred at room temperature for 4 d. Then half the solvent was removed under reduced pressure and toluene (70 cm^3) was added. After 1 h the solution was filtered and the brown crystalline residue was washed with toluene and dried in vacuo (yield, 1.6 g, 79%).

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